

A comparison of measurements from ATMOS and instruments aboard the ER-2 aircraft: Halogenated gases

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Abstract. We compare volume mixing ratio profiles of N_2O , CFC-11, CFC-12, CCl_4 , SF_6 , and HCl in the mid-latitude stratosphere measured by the ATMOS Fourier transform spectrometer with in situ measurements acquired aboard the NASA ER-2 aircraft during Nov 1994. Good agreement is found between ATMOS and in situ correlations of [CFC-11], [CFC-12], and [SF_6] with [N_2O]. ATMOS observations of [CCl_4] are 15% higher than the ER-2 data, but within the systematic uncertainties. ATMOS measurements of [HCl] vs [N_2O] agree to within $\pm 10\%$ of the ER-2 data for [HCl] > 1 ppbv, but exceed in situ observations for smaller [HCl]. ATMOS measurements of [$ClONO_2$] show remarkable agreement with values inferred from in situ observations of [ClO], [NO], and [O₃]. The sum of [HCl] and [$ClONO_2$] observed by ATMOS, supplemented by a minor contribution from [ClO] estimated with a photochemical model, is consistent with the levels of inorganic chlorine inferred from in situ measurements of chlorine source gases.

Introduction

The ATMOS (Atmospheric Trace MOlecule Spectroscopy) Fourier transform spectrometer uses solar occultation measurements to derive volume mixing ratio (VMR) profiles of more than 30 constituents in Earth's atmosphere. During the ATMOS / ATLAS-3 (Atmospheric Labo-ratory for Applications and Science) Space Shuttle mission of Nov 1994, twelve ATMOS occultations, occurring between 4 and 9 Nov 1994, were near-coincident with the mid-latitude (30–51° N) segments of the 2 and 4 Nov flights of the NASA ER-2 aircraft during ASHORE/MAESA (Airborne Southern Hemisphere Ozone Experiment / Measurements for Assessing the Effects of Stratospheric Aircraft). Chang et al. [1996] discuss more fully the geographic coincidence of the observations, compare vertical profiles of [N_2O], and demonstrate good agreement for correlations of long-lived tracers [O₃], [NO_y], [H_2O], and [CH_4] with [N_2O] observed from the two platforms (throughout, [] denotes VMR). This paper presents correlations of [CFC-11], [CFC-12], [CCl_4], [SF_6], and [HCl] with [N_2O] measured from ATMOS and the ER-2, and compares measurements of inorganic chlorine species with results of photochemical model simulations.

All comparisons in this study are presented as correlations with the long-lived tracer N_2O to account for the dynamical histories of different air masses. For the ER-2 flight segments considered here, [N_2O] measured by ATLAS (Airborne Tunable

Laser Absorption Spectrometer) [Loewenstein et al., 1989] are largely within 10% of those observed by ACATS-IV (Airborne Chromatograph for Atmospheric Trace Species) [Elkins et al., 1995]. Because of the higher sampling rate, the ATLAS data for [N_2O] are used for all the ER-2 correlations presented here. Version 2 ATMOS data are used throughout.

Halogen source Gases

ATMOS measures VMRs of CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), HCFC-22 ($CHClF_2$), CH_3Cl , and CCl_4 , which together constitute ~80% of total tropospheric organic chlorine [Zander et al., 1996]. The ACATS-IV gas chromatograph on the ER-2 measures CFC-11, CFC-12, CFC-113 ($CCl_2F-CClF_2$), CH_3CCl_3 , CCl_4 , and Halon-1211 ($CBrClF_2$), which likewise comprise ~80% of tropospheric chlorine. Halogenated gases are measured by ACATS-IV with precisions and accuracies of better than 10% and 7% respectively, at intervals of 3 min, except SF_6 , which is measured every 6 min. ACATS-IV is calibrated on the ground against the same standards used in the National Oceanic and Atmospheric Administration / Climate Monitoring and Diagnostic laboratory network of tropospheric measuring stations [Elkins et al., 1993], and is calibrated in flight by running a sample of air with mixing ratios near stratospheric levels every 4 ambient samples, or 15 to 30 min.

Optical bandpass filters, used to improve the signal-to-noise ratio (SNR) of measured spectra, determine the set of species measured in each ATMOS occultation [Gunson et al., 1996]. All species examined in this paper, except for HCl and N_2O , are detected using transitions below 1000 cm^{-1} , where spectra from Filter 9 (625–2450 cm^{-1}) exhibit degraded SNR compared with those from Filter 12 (625–1400 cm^{-1}). This problem was particularly noticeable during the ATLAS-3 mission (due to the instrumental gain settings) and adversely impacts VMRs retrieved in Filter 9 using a single spectral window below 1000 cm^{-1} , such as CFC-11, CFC-12, CCl_4 , $ClONO_2$, and SF_6 . For these species, only Filter 12 measurements are considered in the present paper. Gases measured in Filter 9 based on fitting either features at higher wavenumbers or an ensemble of spectral windows (e.g., O₃, N_2O , CH_4 , H_2O , NO, NO_2) are unaffected by these difficulties.

Figure 1 illustrates the agreement of ATMOS and ER-2 measurements of [CFC-11] with [N_2O]. The horizontal axis corresponds to altitudes from the upper troposphere to ~30 km. ATMOS measures [CFC-11] with estimated 10% precisions (random errors) of better than 5% and an accuracy (systematic

uncertainty) of 1.1%, and detects $[N_2O]$ with 1σ precisions and accuracies of 5% each. ATMOS makes *a priori* estimates of precision during each VMR retrieval from considerations such as residual errors in the fitting of spectra; systematic uncertainties are determined by combining uncertainties in the spectroscopic band intensities [Brown et al., 1996] with those related to the tangent pressure assignment. More details of ATMOS accuracies and precisions are presented in Abrams et al. [1996]. The mean difference in $[CFC-11]$ measured by ATMOS and the ER-2 is -14.4 (-1.1 pptv of $[(1 \pm 11)]$ at $[N_2O] = 300$ ppbv), well within the uncertainties of the measurements, with no apparent dependence on $[N_2O]$ (throughout, % biases are computed as $[ATMOS/ER-2] / [ATMOS]$). Correlations of $[CFC-12]$ with $[N_2O]$ are shown in Fig. 1b. ATMOS measures $[CFC-12]$ with a 1σ accuracy of 9% and estimated precisions of better than 50%. In mean, good agreement is obtained in $[CFC-12]$ between the ATMOS and ER-2, with differences ranging from +5% (-1.3 pptv of $[CFC-12]$) at $[N_2O] = 170$ ppbv to -6% (-26 pptv of $[CFC-12]$) at $[N_2O] = 280$ ppbv.

Figure 1c compares observations of $[CCl_4]$ vs $[N_2O]$. ATMOS measures $[CCl_4]$ with a 1σ accuracy of 20% and estimated precisions of better than 10%. The ATMOS values of $[CCl_4]$ are 15% higher (20 pptv of $[CCl_4]$ at $[N_2O] = 300$ ppbv) compared to the in situ data. ATMOS retrieves $[CCl_4]$ using the $\nu_3, \nu_1 + \nu_4$ bandhead at 796 cm^{-1} , with temperature-dependent absorption cross-sections and band intensities from Orlando et al. [1992]. The deviation of the ATMOS measurements is consistent with the estimated uncertainty in the band strength, whose reported value varies considerably in the literature [Brown et al., 1996]. Figure 1d shows comparisons of $[SF_6]$ with $[N_2O]$. ATMOS measures $[SF_6]$, a good indicator of the age of stratospheric air owing to its long photochemical lifetime and known tropospheric growth rate, with a accuracy of 1.1% and estimated 1σ precisions of -1.0%. The ATMOS data are on average 5% higher (0.16 pptv of $[SF_6]$ at $[N_2O] = 300$ ppbv) than the in situ observations, demonstrating excellent agreement over a wide range of $[N_2O]$.

Inorganic Chlorine

The coincidence between ATMOS and ER-2 measurements in Nov 1994 provides a test of our understanding of the partitioning of inorganic chlorine (Cl_y) at mid-latitudes. ATMOS measures $[HCl]$ and $[ClONO_2]$, which are the dominant forms of Cl_y in the lower stratosphere for air unaffected by polar stratospheric clouds. Instruments aboard the ER-2 observe $[HCl]$ and $[ClO]$, the latter being the reactive form of Cl_y that photochemically removes ozone. Although ATMOS observes $[HCl]$ and $[ClONO_2]$ using different optical filters and thus never in the same occultation, constituents such as O_3 and N_2O measured in multiple filters provide a framework for combining observations from nearby occultations.

Measured correlations of $[HCl]$ vs $[N_2O]$ are shown in Fig. 2a. ATMOS observes $[HCl]$ in Filter 3 with a 1σ accuracy of 5% and estimated precisions of better than 50% at altitudes above 50 mbar, degrading to 1.5% at 150 mbar. The A-1 IAS (Aircraft Laser Infrared Absorption Spectrometer) diode laser instrument provides in situ observations of $[HCl]$ using transitions in the same spectral band used by ATMOS [Webster et al., 1996]. For the Nov 1994 flights, A-1 IAS reports $[HCl]$ at 6 minute intervals with a 1σ precision of 0.07 ppbv (e.g., 5% at 1.5 ppbv, 20% at 0.35 ppbv) and an accuracy of

5% for $[HCl] > 1$ ppbv, the A-1 IAS observations are 12% lower (0.2 ppbv of $[HCl]$) than the ER-2 data, but the measurements agree within their combined uncertainties. For $[HCl] < 1$ ppbv, the A-1 IAS mixing ratios are lower by 40% (0.4 ppbv of $[HCl]$), although the upper range of variability of the ER-2 data overlaps the ATMOS data. A-1 IAS observations of $[HCl]$ at a given $[N_2O]$ during Nov 1994 were ~60% higher than seen by A-1 IAS in May 1993, when NH mid-latitude $[HCl]/[Cl_y]$ ratios were observed to be -0.4, compared to model calculations of -0.7 [Webster et al., 1994]. This evolution of $[HCl]/[Cl_y]$ sampled by the ER-2 appears correlated with decreasing sulfate aerosol loading [Webster et al., in preparation].

The correlations of $[ClONO_2]$ vs $[N_2O]$ measured by ATMOS and inferred from ER-2 measurements are shown in Fig. 2b. ATMOS detects $[ClONO_2]$ with a accuracy of 20% and estimated 1σ precisions of 10-2000. The peak mixing ratio of $ClONO_2$ equals 0.9 ppbv and occurs at -26 km altitude ($[N_2O]$

170 ppbv), leading to a maximum of -0.5 for the $[ClONO_2]/[HCl]$ ratio. Although in situ measurements of $[ClONO_2]$ have never been obtained, $[ClONO_2]$ can be inferred from noon-time measurements of $[ClO]$, $[NO]$, and $[O_3]$, using the steady-state expressions [Kawa et al., 1992],

$$[ClONO_2]^* = \frac{k_{ClO+NO_2}[ClO][NO_2]}{J_{ClONO_2}} \quad (1)$$

$$[NO_2]^* = [NO] \frac{k_{NO+O_3} + k_{NO+ClO}[ClO]}{J_{NO_2}} \quad (2)$$

where * denotes an inferred quantity and J in these equations refers to concentration (measurements of $[NO_2]$ on the ER-2 are unavailable for the flights under consideration). Photolysis rates for $ClONO_2$ and NO_2 are computed using a radiative transfer model constrained by planetary reflectivity from the Total Ozone Mapping Spectrometer (TOMS) and vertical profiles of O_3 derived by combining in situ observations with total column measurements from TOMS [Salawitch et al., 1994]. A-1 IAS measurements are obtained at sunset, where models indicate $[ClONO_2]$ should fall midway between values at noon and night. Figure 2b shows $[ClONO_2]^*$ (sunset) inferred from the ER-2, calculated from in situ measurements of $[ClO]$, $[NO]$, and $[O_3]$ obtained within ± 2 hr of local noon using Eqs. 1, 2 and $[ClONO_2]^* (\text{sunset}) = [ClONO_2]^* (\text{noon}) + 0.5 [ClO] (\text{noon})$. The 1σ uncertainty in $[ClONO_2]^*$ estimated from the propagation of errors in the kinetic parameters and observed quantities is $\pm 90\%$ [Kawa et al., 1992]. For $[N_2O] < 250$ ppbv, the A-1 IAS measurements of $[ClONO_2]$ and values inferred from the in situ data are 0.0 ± 0.0 average within $\pm 10\%$ (± 0.04 ppbv of $[ClONO_2]$). Systematic discrepancies of $\sim 45\%$ (~ 0.06 ppbv of $[ClONO_2]$) are exhibited at higher values of $[N_2O]$, where the fractional uncertainties in $[ClONO_2]$ measured by ATMOS become large due to its decreasing abundance.

Figure 2c compares $[Cl_y]$ vs $[N_2O]$ from A-1 IAS anti-ER-2 data. The ATMOS values of $[Cl_y]$ were constructed by summing the measured $[HCl]$ and $[ClONO_2]^*$, averaged on a 10 ppbv wide grid of $[N_2O]$, with $[ClO]$ calculated for sunset using the assumptions for Model C described below. The A-1 IAS values of $[Cl_y]$ were determined by averaging and summing, on the same $[N_2O]$ grid, measurements of $[HCl]$, $[ClONO_2]^* (\text{noon})$, and $[ClO]$ collected within ± 2 hr of local noon. The contribution of $[ClO]$ to $[Cl_y]$ is less than 50% for all cases considered here. Observations [Zander et al., 1996] and

photochemical simulations indicate that other gases, such as HCl , contribute negligibly to $[\text{Cl}_y]$ at these altitudes.

Figure 2c includes another estimate of inorganic chlorine, denoted here as $[\text{Cl}_y]^{\dagger}$, determined by subtracting total organic chlorine measured by ACATS and the Whole Air Sample during the 1992 ER-2 campaign from the total organic chlorine loading in the troposphere [Woodbridge et al., 1995]. The $[\text{Cl}_y]^{\dagger}$ relation shown here has been increased by 6.7% relative to the published relation of Woodbridge et al. to account for changes in stratospheric chlorine between 1992 and Nov 1994 [Zander et al., 1996]. ATMOS $[\text{Cl}_y]$ are on average 0.25 ppbv lower than levels predicted from in situ measurements of organic source gases for $[\text{N}_2\text{O}] > 180$ ppbv, with better agreement at lower $[\text{N}_2\text{O}]$. Inferred $[\text{Cl}_y]$ from the ER-2 are on average 0.58 ppbv lower than $[\text{Cl}_y]$. The smaller abundance of $[\text{Cl}_y]$ from the in situ measurements of inorganic chlorine compared to $[\text{Cl}_y]$ from ATMOS is due to lower values of $[\text{HCl}]$ that are not balanced by higher $[\text{ClONO}_2]$. Trajectory calculations indicate that air parcels along these ER-2 flights have recently undergone large excursions in temperature (~ 15 K) and latitude ($\sim 15^\circ$) [P. Newman, private communication, 1996]. However, our model simulations show the partitioning of $[\text{HCl}]$ and $[\text{ClONO}_2]$ is insensitive to changes in temperature and latitude experienced along these trajectories, provided precursor (i. e., Cl_y , NO_y , H_2O , O_3) levels remain unchanged. It is unlikely that the air sampled by ATMOS and the ER-2 could have large differences in $[\text{Cl}_y]$ for the same $[\text{N}_2\text{O}]$, given the similarity of source gases displayed in Fig. 1. The cause of the discrepancy between ATMOS and ER-2 measurements of $[\text{HCl}]$ remains unclear.

Photochemical simulations [Salawitch et al., 1994; Michelsen et al., 1996] are used to test our understanding of partitioning of inorganic chlorine gases. The model is constrained to match calculated $[\text{HCl}]$ and $[\text{ClONO}_2]$ to the sum measured by ATMOS. Two sets of kinetic parameters are considered: the first uses reaction rate constants and photolytic cross sections from the JPL 1994 compilation [DeMore et al., 1994] and a 0% HCl yield from the reaction $\text{ClO} + \text{O}_3$; the second ('Model C' of Michelsen et al. [1996]) incorporates several changes of which the most significant with respect to partitioning of $[\text{ClONO}_2]$ and $[\text{HCl}]$ is an assumed 7% yield of HCl from the reaction $\text{ClO} + \text{O}_3$. The sensitivity of model results to each kinetic parameter is discussed in Michelsen et al. [1996].

Model results for $[\text{HCl}]$ and $[\text{ClONO}_2]$ at local sunset are compared with ATMOS observations in Figs. 2a and 2b. For $[\text{N}_2\text{O}] > 200$ ppbv, both models predict similar levels of $[\text{HCl}]$ and are consistent with the partitioning of $[\text{ClONO}_2]$ and $[\text{HCl}]$ observed by ATMOS. At lower levels of $[\text{N}_2\text{O}]$, the model allowing for production of HCl from $\text{ClO} + \text{OH}$ results in better agreement with the ATMOS data. Figure 2d shows a comparison of $[\text{ClO}]$ calculated subject to constraints imposed by the ATMOS data, but coil-cspotting to mid-afternoon solar conditions sampled by the ER-2, where in situ measurements of $[\text{ClO}]$ are obtained with a 1 σ accuracy of 15% [Stimpfle et al., 1994]. Although both models overestimate $[\text{ClO}]$ for $[\text{N}_2\text{O}] < 240$ ppbv, data for $[\text{ClO}]$ agree more closely with the model that allows ferrr production of $[\text{HCl}]$ from $\text{ClO} + \text{OH}$.

The decade-long record of ATMOS observations of organic and inorganic chlorine allows quantification of distributions and trends for gases that are precursors of ozone destroying

radicals and significant contributors to greenhouse warming [Zander et al., 1996]. ATMOS measurements provide a self-consistent picture of the organic and inorganic chlorine budgets and, together with in situ data, provide valuable constraints on our understanding of chlorine chemistry and the effects of industrially derived chlorine compounds on ozone.

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References

- Abrams, M. C. et al., 011 the assessment and uncertainty of atmospheric trace gas burden measurements with high resolution in frared solar occultation spectra from space, *Geophys. Res. Lett.*, this issue, 1996.
- Brown, L. R., M. R. Gunson, R. A. Toth, P. W. H. Wilson, and C. P. Rinsland, The 1995 Atmospheric Trace Molecule Spectroscopy (ATMOS) line list, *Appl. Opt.*, in press, 1996.
- Chang, A. Y. et al., A comparison of measurements from ATMOS and instruments aboard the ER-2 aircraft: Tracers of atmospheric transport, *Geophys. Res. Lett.*, this issue, 1996.
- DeMore, W. B. et al., Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation number 11, NASA, JPL Publication 94-96, 1994.
- Elkins, J. W. et al., Decrease in the growth rates of atmospheric chlorofluorocarbons 11 and 12, *Nature*, 364, 75 (1993).
- Elkins, J. W. et al., Airborne gas chromatograph for in situ measurements of long-lived species in the upper troposphere and lower stratosphere, *Geophys. Res. Lett.*, 23, 347-350, 1996.
- Fahey, D. W. et al., In situ measurements of total reactive nitrogen, total water, and aerosol in a polar stratospheric cloud in the Antarctic, *J. Geophys. Res.*, 94, 11299-11315, 1989.
- Kawa, S. R. et al., Photochemical partitioning of the reactive nitrogen and chlorine reservoirs in the high-latitude stratosphere, *J. Geophys. Res.*, 97, 7905-7923, 1992.
- Loewenstein, M., J. R. Podolske, K. R. Chan, and S. I. Strahan, Nitrous oxide as a dynamical tracer in the 1987 Airborne Antarctic Ozone Experiment, *J. Geophys. Res.*, 94, 11589-11598, 1989.
- Michelsen, H. A. et al., Stratospheric chlorine partitioning: Constraints from shuttle-borne measurements of HCl , ClONO_2 , and ClO , *Geophys. Res. Lett.*, this issue, 1996.
- Orlando, J. J., G. S. Tyndall, A. Huang, and J. G. Calvert, Temperature dependence of the infrared absorption cross sections of carbon tetrachloride, *Geophys. Res. Lett.*, 19, 1005-1008, 1992.
- Proffitt, M. H. et al., In situ ozone measurements within the 1987 Antarctic ozone hole from a high-altitude 11 (-2 aircraft, *J. Geophys. Res.*, 94, 16541-16555, 1989.
- Salawitch, R. J. et al., The distribution of hydrogen, nitrogen, and chlorine radicals in the lower stratosphere: implications for changes in O_3 due to emission of NO_y from supersonic aircraft, *Geophys. Res. Lett.*, 21, 2541-2550, 1994.
- Stimpfle, R. M. et al., The response of ClO radical concentrations to variations in NO_2 radical concentrations in the lower stratosphere, *Geophys. Res. Lett.*, 21, 2543-2546, 1994.
- Webster, C. R. et al., Hydrochloric acid and the chlorine budget of the lower stratosphere, *Geophys. Res. Lett.*, 21, 2575-2578, 1994.
- Woodbridge, E. L. et al., Estimates of total organic and inorganic chlorine in the lower stratosphere from in situ and flask measurements during AASE-II, *J. Geophys. Res.*, 100, 3057-3064, 1995.
- Zander, R. et al., The 1994 northern midlatitude budget of stratospheric chlorine derived from ATMOS/ATLAS 3 observations, *Geophys. Res. Lett.*, this issue, 1996.

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Figure Captions

Figure 1. Correlations of $[(1-1)], [CFC-12], [CCl_4]$, and $[SF_6]$ vs $[N_2O]$ measured by ATMOS and instruments aboard the ER-2 aircraft: $[N_2O]$ (ATLAS), Loewenstein et al.; $[CFC-11]$, $[CFC-12]$, $[CCl_4]$, and $[SF_6]$ (ACATS-IV), Elkins et al. ATMOS error bars reflect estimated precision; systematic uncertainties are discussed in the text.

Figure 2. Correlations of $[11(3)]$, $[ClONO_2]$ or $[ClONO_2]^*$, $[Cl_y]$, $[HCl] + [ClONO_2] + [ClO]$, and $[ClO]$ vs $[N_2O]$ from ATMOS and ER-2 measurements: $[N_2O]$ (ATLAS), Loewenstein et al.; $[HCl]$ (ATLAS), Webster et al.; $[ClO]$, Stimpfle et al. ER-2 $[ClONO_2]^*$ is inferred for sunset from noontime $[ClO]$, $[NO]$ (Fahey et al.), and $[O_3]$ (Proffitt et al.). ATMOS $[Cl_y]$ includes calculated $[ClO]$. ATMOS error bars reflect estimated precision, except for the third panel, where ATMOS and ER-2 error bars represent the standard deviation of the components of $[Cl_y]$, averaged over equally spaced intervals of $[N_2O]$. JPL94 [DeMore et al.] and Model C [Michelsen et al.] assume yields of 0% and 7%, respectively, for HCl from $ClO + OH$.

Figure 1. Correlations of $[CFC-11]$, $[CFC-12]$, $[CCl_4]$, and $[SF_6]$ vs $[N_2O]$ measured by ATMOS and instruments aboard the ER-2 aircraft: $[N_2O]$ (ATLAS), Loewenstein et al.; $[CFC-11]$, $[CFC-12]$, $[CCl_4]$, and $[SF_6]$ (ACATS-IV), Elkins et al. ATMOS error bars reflect estimated precision; systematic uncertainties are discussed in the text.

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